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THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

On the Velocity of Sound in Gases at High Temperatures, and the Ratio of the Specific Heats.

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The experiments described in this memoir on the velocity of sound in gases, at temperatures varying from atmospheric to that of a bright red heat, were made with the object of tracing the change in the specific heat of gases with rising temperature, and, if possible, of arriving at formulæ which might be applicable to the extremely high temperatures reached in explosions. The sound method was decided on chiefly for the reasons (1) that the velocity of sound in a heated gas gives a value for the ratio of the two specific heats at the temperature of the experiment, and not as in the method of mixtures at a mean temperature between the highest and lowest point of the heated and cooled gas; and (2) because we had had considerable experience in the use of a chronograph for measuring the rapid movements of flame through gases in long tubes.

It is necessary to make it clear at starting that no claim is made that these experiments give more exact determinations of the specific heat of gases than those given previously by experiments over low ranges of temperature; the object has been to obtain by comparative measurements the general gradients of the curves rather than to find the exact value at any definite point.

The method of mixtures, in which a known volume of the heated gas is passed into a calorimeter (originally used by Delaroche* and Bérard, and improved by Regnault† and Wiedemann‡), has been employed by Holborn§

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* 'Annales de Chimie,' vol. 85, p. 721 (1813).

† 'Mem. de l'Acad. Paris,' vol. 26, p. 1 (1862).

‡ 'Pogg. Ann.,' vol. 157 (1876).

§ 'Sitzber. Preuss. Akad. Berlin,' 1905, p. 175.

and Austin for high temperatures. Swann* determined the specific heats of air and of carbon dioxide at 20° and 100° C. at constant pressure by measuring the rise of temperature of the gas after passing over a coil of platinum wire, heated electrically by a current of known constant value.

The most successful direct determinations of the specific heats of gases at constant volume were made by Joly.† A metal vessel, which was allowed to swing freely in an outer jacket, was carefully weighed by suspension from the pan of a delicate balance. A current of dry steam was then passed through the outer jacket, until the weight of the metal vessel had increased to a constant maximum by the condensation of steam on its surface. The difference between the values obtained when the vessel was evacuated and when full of gas gave a measure of the heat capacity of the gas itself. The method is not suitable for determinations at temperatures much higher than the boiling point of water.

With the object of determining the specific heats of gases at constant volume at very high temperatures, Berthelot‡ and Vieille and Mallard§ and Le Chatelier made use of an explosion method. They fired gaseous mixtures of known composition in metal bombs, and from the pressures registered, combined with the known heats of reaction, calculated the heat capacities of the gaseous products.

The methods of pressure-measurement have since been improved by Langen|| and by Hopkinson¶; and further improvements have been made in the explosion-method by M. Pier** and by Bjerrum,†† who has calculated the specific heats of nitrogen, carbon dioxide, and steam up to 3000° from his own experiments and from those of Holborn and of Pier.

The method of adiabatic expansion originally devised by Clément‡‡ and Désormes has been improved by Röntgen§§ and modified by Lummer|||| and Pringsheim. It has given good results for steam and carbon dioxide in the

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* 'Phil. Trans.,' A, vol. 210, p. 199 (1910).

† 'Phil. Trans.,' A, vol. 182, p. 73 (1892).

‡ 'Compt. Rend.,' vol. 95, p. 1280 (1882); vol. 96, pp. 116, 1218, 1358 (1883); 'Ann. Chim. Phys.,' vol. 4, p. 1379 (1885).

§ 'Ann. des Mines,' vol. 4, p. 379 (1884).

|| 'Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens, Berlin,' vol. 8 (1903).

¶ 'Proc. Inst. Mech. Eng.,' 1908.

** 'Zeitsch. Phys. Chem.,' vol. 62, p. 385 (1908); 'Zeitsch. f. Electrochem.,' vol. 15 (1909); vol. 16 (1910).

†† 'Zeitsch. Phys. Chem.,' vol. 79 (1912); 'Zeitsch. f. Electrochem.,' vol. 17 (1911); vol. 18 (1912).

‡‡ 'Journ. de Phys.,' vol. 89 (1819).

§§ 'Pogg. Ann.,' vol. 148, p. 580 (1873).

|||| 'Wied. Ann.,' vol. 64, p. 553 (1898).

hands of Makower[*] and of Partington,[†] but it has not been used for determinations at high temperature.

Maneuvrier,[‡] on the other hand, has used this method of adiabatic compression, measuring the volume and pressure produced by the rapid descent of a piston in a cylinder full of gas, while Clerk[§] has measured the rise of temperature when a known amount of work was done on the gas in a gas engine. More recently, Crofts[||] has attempted to determine the ratio of the specific heats of hydrogen, nitrogen, and carbon dioxide by measuring the minimum adiabatic compression necessary to fire electrolytic gas diluted with equal volumes of these gases, and of argon, on the assumption that the ignition temperatures of such mixtures were identical.

The first determinations of the velocity of sound in a gas were made in free air, in 1738, by Cassini, Maraldi, and La Caille, of the Paris Academy, by direct measurement. In 1829 Dulong[¶] determined the velocity of sound in different gases by measuring the pitch produced by blowing an organ-pipe in the several gases—a method first suggested by Bernoulli in 1762.

Kundt's[**] method, in which stationary waves are produced in a tube containing fine dust, has been used by Wüllner,[††] Strecker,[‡‡] Capstick,[§§] and others. Stevens[||||] and Kalähne[¶¶] used a resonance method suggested by Quincke. Similar methods were afterwards developed by Seebeck,[***] Low,[†††] and by Thiesen[‡‡‡] and Steinwehr.

Experimental.

In the experiments described in this paper, direct measurements of the time taken by a sound wave to travel through the gas, contained in a tube of known length, were made by means of a pendulum chronograph. The sound was propagated through pipes of three different materials—lead, mild steel, and silica.

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[*] 'Phil. Mag.' [6], vol. 5, p. 226 (1903).

[†] 'Physik. Zeit.,' vol. 14, p. 969 (1913).

[‡] 'Ann. Chim. Phys.' [7], vol. 6, pp. 321, 377 (1895).

[§] 'Roy. Soc. Proc.,' A, vol. 82 (1909).

[||] 'Trans. Chem. Soc.,' vol. 107, pp. 290, 306 (1915).

[¶] 'Pogg. Ann.,' vol. 16, p. 438 (1829).

[**] 'Pogg. Ann.,' vol. 135, pp. 337, 527 (1868).

[††] 'Wied. Ann.,' vol. 4, p. 321 (1878).

[‡‡] 'Wied. Ann.,' vol. 13, p. 20 (1881); vol. 17, p. 85 (1882).

[§§] 'Roy. Soc. Proc.,' vol. 34, p. 101 (1893).

[||||] 'Ann. d. Physik.,' [4], 7, 285 (1902).

[¶¶] 'Ann. d. Physik.,' vol. 11, p. 225 (1903).

[***] 'Pogg. Ann.,' vol. 139, p. 104 (1870).

[†††] 'Wied. Ann.,' vol. 52, p. 641 (1894).

[‡‡‡] 'Ann. d. Physik.,' vol. 25, p. 506 (1908).

Preliminary experiments made in tubes up to 25 mm. in diameter showed that a sound wave traversed the length of a coiled tube—as measured along the axis—in the same time as it travelled through the tube when straight. It was not found possible to coil a lead pipe round a drum without appreciably increasing its length; so that, when a long coiled tube was employed, it was measured as it was wound on the drum layer by layer. In all cases the lengths of the tubes were measured along their axes.

In each case the tube was fitted at its two ends with exactly similar aluminium end-pieces, each of which acted as transmitter and receiver in turn. By this means the sound wave could be sent first in one direction and immediately afterwards in the other direction through the tube. By a simple switch arrangement each end-piece could be connected with either of the two magnetic styles of the chronograph, so that each style could be used alternately to mark the start and the finish of the sound wave's course. The end-pieces were closed at one end with a thin steel plate, and were fitted with a small disc of platinum, which broke an electric circuit when bent by the passing sound wave. The construction of this apparatus is shown in section in fig. 1.

The sound wave was produced by the steel tympanum (T) when struck by the hammer of the electromagnet (M). As the wave travelled along the tube it raised the disc of platinum (P) which covered a circular opening in the aluminium; this platinum disc was kept in position by three aluminium washers, the top one of which was screwed down. A platinum upright (G), 1 cm. long, welded into the centre of the disc, carried a capillary tube of glass which passed up through the centre of a cylinder of graphite (C). The upper end of this glass tube was bent over through 180° and carried a fine

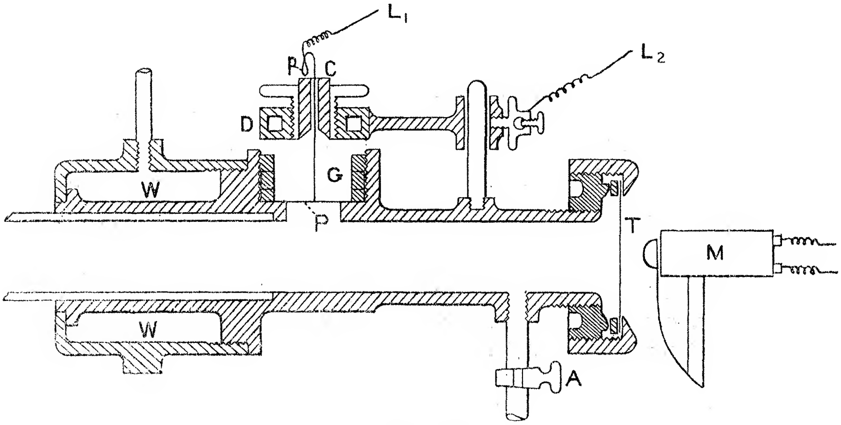

Fig. 1.

platinum wire made into the form of a loop (*p*). The height of the graphite could be adjusted by means of the brass sleeve in which it was held, so as to bring it into light contact with the platinum loop, thus making connection between the two copper leads (L_1) and (L_2) which were in circuit with one of the chronograph styles. The whole end-piece was kept cool by a stream of cold water passed through (W) and (D). This cooling was necessary, since if the graphite became heated, sparking from the platinum point made indentations on its surface causing the contact to work irregularly. It was found that the efficiency of the contact was greatly increased by electroplating the graphite surface with a thin layer of copper. The gases were admitted rapidly to the tube through the tap A, until the previous contents had been completely swept out through the corresponding tap at the other end; a slow stream was then maintained under a pressure slightly above that of the atmosphere. Immediately before the experiment the taps were turned off and the platinum graphite contacts were adjusted.

The chronograph and electromagnetic styles were the same as those used by Dixon* in his determination of the velocities of detonation waves. The chronograph consisted of a heavy pendulum which carried a smoked glass plate. The pendulum was released by a spring catch and as it passed through the lowest point of its path it caught a "break" which was in circuit with one of the hammers. The chronograph was calibrated by recording on the smoked plate the movements of a standardized tuning fork vibrating 100 times per second. By drawing an arc cutting the tuning fork marks and measuring the lengths of the chords for 1, 2, 3 or more complete vibrations, the distances corresponding with 0·01, 0·02, 0·03, etc., second, for every position on the plate, were determined and mapped out. From this "map" the value in time of any measured chord could be found by inspection. The chronograph was recalibrated from time to time with the tuning fork.

Before a sound wave was passed through the tube, a "preliminary experiment" was always performed. For this purpose, a current from two storage cells was made to pass in series through the two style magnets, the "break" on the chronograph table, and through a resistance which was so adjusted that the current passing through each magnet was of the same value in this "preliminary experiment" as in the experiments which were to follow. The pendulum was released and the consequent breaking of the circuit caused each style to rise and record its mark on the moving plate. Each mark was affected by the retardation of the corresponding electromagnet and the velocity with which the style was lifted by the spring operating it.

The first style was then connected in series with one storage cell and the first platinum graphite contact; and the second style was similarly connected with the second contact at the opposite end of the tube. At the same time a current was made to pass in series through the electromagnet holding the first hammer and through the contact "break" of the chronograph. The pendulum was then allowed to fall, and during its path broke the circuit operating the hammer, which accordingly produced the sound wave. This wave bent the first platinum disc thereby breaking the circuit and releasing the first style. The wave then passed through the tube, bent the second platinum disc and so released the second style. The two marks recorded were affected by the same retardations as in the preliminary experiment. The distance between the two marks made by the first style represented the interval of time between the releasing of the hammer and the raising of the first disc; and the distance between the marks of the second style represented the time interval between the release of the hammer and the raising of the second disc. The difference between these time-intervals was, therefore, the time taken by the sound wave to travel from the first disc to the second. The experiment was repeated by sending the sound wave from the other end of the tube. The connections were then rearranged so that the first style was in series with the second contact and the second style in series with the first contact, and the sound wave was again measured in both directions.

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* 'Phil. Trans.,' A, vol. 184, p. 97 (1893).

The mean of the four experiments gave one determination in which all errors due to magnet and spring retardations were eliminated. Several determinations in close agreement were required before any series of experiments was considered satisfactory.

Preparation of the Gases.

Nitrogen was prepared by slowly dropping a concentrated solution of sodium nitrite into a hot concentrated solution of ammonium sulphate containing potassium dichromate. The gas was purified by passing through dilute sulphuric acid to remove ammonia and through ferrous sulphate to remove oxides of nitrogen, and was dried by calcium chloride and concentrated sulphuric acid.

Carbon dioxide was obtained from dilute hydrochloric acid and marble chippings; it was washed free from acid by sodium carbonate solution and was dried by calcium chloride and concentrated sulphuric acid.

Nitrous oxide was prepared by carefully heating pure ammonium nitrate, and was purified by washing with ferrous sulphate solution and drying with calcium chloride.

Methane was prepared by the decomposition of comparatively pure aluminium carbide with hot water, and was purified according to the method described by Campbell* and Parker.

Ethane was prepared by the action of water on magnesium ethyl iodide, and also by the action of ice-water on zinc ethide.

Argon was obtained from the atmosphere by first passing air freed from moisture and carbon dioxide over heated copper turnings; the remaining gas was then passed into a previously evacuated cylindrical iron vessel containing a finely powdered mixture of nine parts by weight of calcium carbide and one part of calcium chloride. The iron vessel was heated to about 800° C. in an electric furnace. The unabsorbed gas was pumped off and passed over heated calcium, to remove the last traces of oxygen and nitrogen. The resulting gas (which was practically pure argon) was stored over mercury and no attempt was made to remove the small quantities of other inert gases present. Density determinations of the product confirmed the absence of any appreciable quantity of light gases.

Experiments in Lead Tubes.

For experiments up to 100° C. it was most convenient to use a coil of lead pipe immersed in a large iron water-bath, which could be heated to the boiling point by a ring of gas-burners. The two ends of the pipe emerged through slots in the lid just far enough to make junction with the cooled end-pieces, the exposed portions of the lead (only a few centimetres) being wrapped in asbestos. In experiments made above the room temperature the mean time-intervals recorded on the chronograph were corrected for the distance travelled by the sound in the two cooled end-pieces.

As an illustration of the readings obtained, we may instance the determination of the velocity of sound in carbon dioxide at 100° C., measured in a lead pipe 25 mm. in diameter. In the readings under A and A_1 the sound was sent in one direction through the tube, in those under B and B_1 the sound was sent in the other direction; between A and A_1 and between B and B_1 the chronogragh connections were reversed. After each group of four readings had been taken, a fresh smoked plate was inserted in the pendulum and the process repeated—care being taken that the tracings were, as nearly as possible, in the same positions on the plate:—

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* 'Trans. Chem. Soc.,' vol. 103, p. 1292 (1913).

June 16, 1914.	A.	B.	B_1.	A_1.	Mean.
					mm.
Time—4 h. 10 m.	190·0	192·1	190·9	189·1	
	29·9	30·1	28·6	29·9	
	160·1	162·0	162·3	159·2	= 160·90
Time—4 h. 15 m.	189·5	190·6	190·6	188·5	
	30·0	29·4	29·4	28·4	
	159·5	161·2	161·2	160·1	= 160·50
Time—4 h. 21 m.	190·6	191·6	190·6	189·9	
	30·5	30·0	29·1	29·9	
	160·1	161·6	161·5	160·0	= 160·80
Time—4 h. 31 m.	190·0	192·1	190·0	188·0	
	30·0	30·0	29·0	28·5	
	160·0	162·1	161·0	159·5	= 160·65
Time—4 h. 36 m.	188·0	191·4	191·5	189·2	
	28·5	30·0	29·3	29·3	
	159·5	161·4	162·2	159·9	= 160·75
				Average	160·72

It was not found necessary to calculate the rate from each of the five sets of markings, as their respective positions on the several plates were practically the same; it was sufficient to take the *mean* distance traversed by the pendulum per 0·01 second (while the styles were tracing these marks) in order to calculate the velocity of the sound wave from the average of the group-readings. Thus the length of the tube being 18·91 metres, and the mean distance traversed by the pendulum per 0·01 second being 25·30 mm., the average velocity of sound in the gas per second is

$$\frac{18{\cdot}91 \times 0{\cdot}0253 \times 100}{0{\cdot}16072} = 297{\cdot}7 \text{ m.}$$

But a small correction is necessary for the two cooled ends of the pipe, of which 15 cm., or 0·8 per cent., were kept at 20° C. At this temperature the velocity of sound in carbon dioxide is 266 m.p.s., and therefore the velocity at 100° C. is:—

$$V = \frac{297{\cdot}7 \times 99{\cdot}2 \times 266}{26600-(0{\cdot}8 \times 297{\cdot}7)} = 298{\cdot}0.$$

In a similar experiment, made with a slightly shorter tube and with longer cooled ends, the following readings were obtained:—

February 10, 1915.	A.	B.	B_1.	A_1.	Mean.
					mm.
Time—5 h. 10 m.	184·5 25·3	183·6 26·1	183·6 25·8	184·0 25·3	
	159·2	157·5	157·8	158·7	= 158·3
Time—5 h. 15 m.	183·8 25·5	182·6 25·8	182·6 25·8	183·0 24·9	
	158·3	156·8	156·8	158·1	= 157·5
Time—5 h. 18 m.	183·6 24·9	183·6 25·9	182·1 25·0	183·6 25·3	
	158·7	157·7	157·1	158·3	= 157·95
Time—5 h. 22 m.	184·0 25·1	182·7 25·6	182·7 25·5	183·0 24·2	
	158·9	157·1	157·2	158·8	= 158·0
Time—5 h. 26 m.	183·5 25·5	183·1 25·4	181·2 24·4	182·4 25·0	
	158·0	157·7	156·8	157·4	= 157·5
				Average	157·85

The length of the tube being 18·58 metres, and the mean distance traversed by the pendulum per 0·01 second being 25·30 mm., the average velocity of sound per second is

$$\frac{18\cdot58\times0\cdot0253\times100}{0\cdot15785}=297\cdot6\text{ m.}$$

The portion of the tube outside the bath and cooled to 10° C. was 1·6 per cent. of the total length, the corrected velocity is therefore:—

$$V=\frac{297\cdot6\times98\cdot4\times262}{26200-(1\cdot6\times297\cdot6)}=298\cdot3.$$

A similar set of readings give, when corrected, a velocity of 298·7 m.p.s. So we have taken the mean of the three sets, viz., 298·3 m.p.s., as the velocity of sound in the lead tube at 100° C. In Table I are given the

Table I.—Velocity of Sound in Gases in Lead Tube.

Temperature (by mercury thermometer).	Velocity in metres per second in			
	Air.	Carbon dioxide.	Methane.	Ethane.
° C.				
10	334·4	262·2	431·8	305·8
50	355·5	279·3	454·0	325·1
100	385·1	298·3	481·7	346·5

mean velocities obtained in the lead tubes at room temperature, 50° C., and 100° C. in air, carbon dioxide, methane, and ethane.

Experiments in a Steel Tube.

For higher temperatures a coiled tube of mild steel, 14·70 metres in length and 28 mm. in diameter, was used.

The steel pipe (fig. 2) was packed in fine sand and in an annular iron vessel, D, which was let down into a furnace between the central cylindrical block of fire-clay, A (12 inches in diameter), and the circular fire-clay wall, B (3 inches in thickness), attached to a sheet-iron cylinder, 2 feet 6 inches in diameter. A lid of fire-clay, C, attached to an iron case rested on the top of the fire-clay centre-piece and walls. The flames from a ring of eighteen Bunsen burners passed upwards between the central fire-clay block and the tube-case, the products of combustion passing downwards between the outer side of the tube-case and the fire-clay walls. On reaching the bottom of the furnace the hot gases passed through a series of openings into an outer passage between the furnace and an asbestos-lined iron sheath, E, and so to the chimney in the middle. Through the top of the furnace iron tubes were inserted, so that the platinum resistance-thermometers might be pushed down through the sand in the tube-cases to different depths on either side.

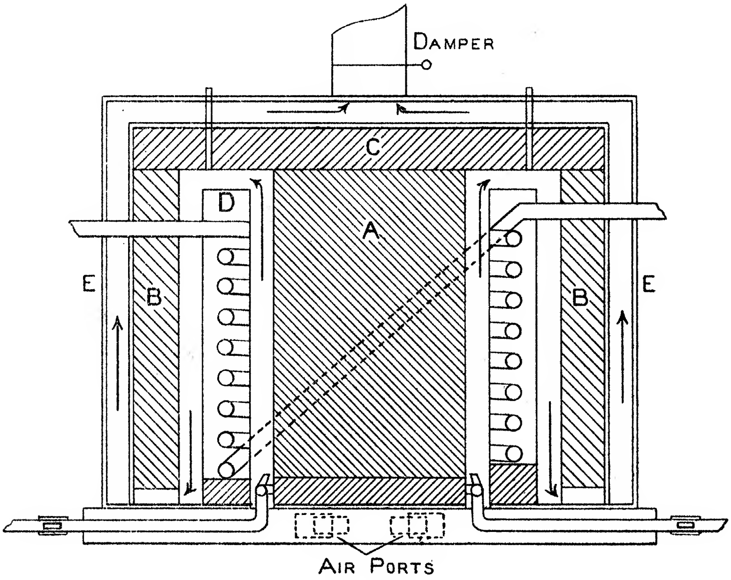

FIG. 2.

The two ends of the steel tube were brought out of the furnace through slots in the fire-clay walls which were then made practically gas-tight by a packing of asbestos, that allowed sufficient "play" for the expansion of the tube.

The gas supply to the burners was carefully governed, and the air mixing with the gas could be regulated. The whole air supply to the furnace could be cut off by closing the air ports in the iron stand, in which a movable sector allowed access to the ring of burners. The chimney draught could be regulated or entirely stopped by a diaphragm.

The furnace, constructed by Messrs. Fletcher, Russell, and Co., was designed to maintain a temperature of 1100° C., and this temperature could be reached with a good gas supply and the burners full on. In practice it was not found possible to keep the upper part of the tube at the same high temperature as the lower portion when the flames were burning, a difference of 10° to 15° C. being registered between the upper and lower coils. On turning off the gas the lower portion cooled more quickly than the upper, owing to the draught of cold air from below. When, however, the air supply was completely cut off by closing the air ports, the cooling was much slower, the upper portion of the coil remaining nearly constant until the lower portion had fallen to the same temperature. By raising the temperature of the lower portion some 25° above the point desired, and then turning off the gas and closing all ports, the upper and lower coils reached a common temperature some 10° above the desired point, and then cooled very nearly at the same rate.

The velocities of sound were therefore measured—during this constant cooling period—from a few degrees above to a few degrees below the standard temperature aimed at, and the mean result was taken as the velocity at that temperature.

In making the determinations one observer worked the chronograph while the second attended to the contacts and the third noted the temperature-readings, as nearly as possible at intervals of two minutes. This allowed time to make measurements of the sound in both directions at, or very close to, each recorded temperature.

The following readings were obtained with nitrogen at 800° C., 900° C., and 1000° C.:—

Temperature.	Mean chronograph reading.	Temperature.	Mean chronograph reading.	Temperature.	Mean chronograph reading.
° C.	mm.	° C.	mm.	° C.	mm.
808	58·8	906	56·9	1008	54·8
804	59·2	901	57·1	1002	55·0
800	59·2	898	57·2	997	55·4
790	59·4	896	57·4	992	55·1
800	59·15	900	57·15	1000	55·08

When allowance is made for the expansion of the steel coil at 1000° and for the distance traversed by the pendulum in 1/100 second, the average velocity of sound in the tube is found to be

$$\frac{14{\cdot}70 \times 1{\cdot}012 \times 0{\cdot}0256 \times 100}{0{\cdot}05508} = 691{\cdot}4 \text{ m.p.s.}$$

If this velocity is corrected for the cooled ends of the tube, of which it was estimated that 1·08 per cent. was at the mean temperature of 100°, then

$$V = \frac{691{\cdot}4 \times 98{\cdot}92 \times 390}{39000-(1{\cdot}08 \times 691{\cdot}4)} = 697{\cdot}3 \text{ m.p.s.}$$

The average velocity at 900° C. is given by

$$\frac{14{\cdot}70 \times 1{\cdot}0108 \times 0{\cdot}0256 \times 100}{0{\cdot}05715} = 665{\cdot}3 \text{ m.p.s.}$$

and correcting for the cooled ends of the tube assumed to have a mean temperature of 90°,

$$V = \frac{665{\cdot}3 \times 98{\cdot}92 \times 385}{38500-(1{\cdot}08 \times 665{\cdot}3)} = 670{\cdot}7 \text{ m.p.s.}$$

The average velocity at 800° C. is given by

$$\frac{14{\cdot}70 \times 1{\cdot}0096 \times 0{\cdot}02558 \times 100}{0{\cdot}05915} = 641{\cdot}8 \text{ m.p.s.}$$

and correcting in a similar manner

$$V = \frac{641{\cdot}8 \times 98{\cdot}92 \times 382}{38200-(1{\cdot}08 \times 641{\cdot}8)} = 646{\cdot}6 \text{ m.p.s.}$$

Of these three determinations we felt most confidence in the value obtained at 900°; this value was afterwards found to agree very closely with the value determined in the silica tube at 905°.

Measurements made up to 300° with other gases were corrected in a similar manner. In this way the velocity of sound in argon and nitrous oxide as well as in nitrogen were measured.

Table II contains the mean results of the experiments with nitrogen and argon.

Table II.—Steel Tube. Velocity of Sound in Nitrogen and in Argon.

Temperature (Pt. resistance thermometer).	Velocity in metres per second.	
	In nitrogen.	In argon.
° C.		
18	345 ·1	311 ·4
300	479 ·0	437 ·0
800	646 ·6	
900	670 ·7	
1000	697 ·3	

In Table III are given the velocities of sound in nitrous oxide as compared with the mean velocities in carbon dioxide as measured in this and in other tubes:—

Table III.—Velocity of Sound in Carbon Dioxide and in Nitrous Oxide.

Temperature.	Velocity in metres per second.	
	In carbon dioxide.	In nitrous oxide.
° C.		
20	265·0	266·0
100	297·8	299·8
200	333·4	335·6
300	364·7	369·2

Experiments in a Silica Tube.

Measurements at high temperatures could not be made for air and carbon dioxide owing to the action of these gases on the metal.

It was, therefore, decided to replace the iron tube by one of silica which could be heated electrically. The difficulties of making a coiled tube of silica 14 to 15 metres long, free from constrictions and strong enough to stand the necessary strains were great; but the Thermal Syndicate of Newcastle-on-Tyne decided to attempt the task. The first two tubes were broken in transit. The third arrived in good condition, was wound with platinum wire and suspended in an iron case, but broke in several places on heating.

The fourth and final tube proved more satisfactory. It was 14·5 metres long, 25 mm. internal diameter, and made into a spiral of seven complete turns, the end sections being curved outwards in opposite directions. This coil was measured into sixteen equal sections and each section was wound with the same length of platinum wire, the turns of wire being 6 mm. apart. It was then supported on four short lengths of stout silica tube, which were suspended freely inside a rectangular iron box (1·8 m. × 1·4 m. × 1·36 m.) from a horizontal cross-bar of iron (fig. A). The ends of the platinum wire were connected by leads of nichrome to two switchboards, one at the front and the other at the back of the furnace. The iron box was then filled with kieselguhr.

One end of the silica coil projected a short distance through a hole in the front of the iron case, while the other end came through the back. To each end the aluminium end-piece (already described) was attached, the joint between silica and aluminium being made with cement.

The current used for heating the coil was obtained from a 200 volt supply and was regulated by means of a resistance frame of a maximum resistance of 50 ohms which was immersed in oil and kept cool by an external water-bath.

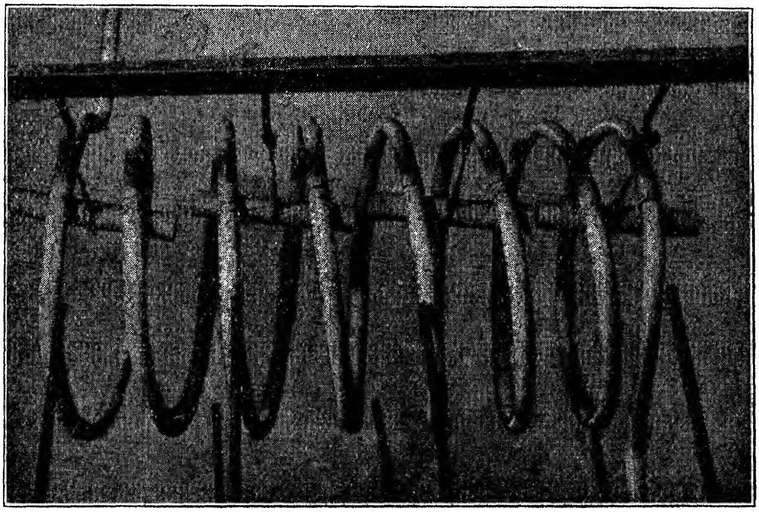

Fig. A.—Wound silica tube, showing method of suspension before kieselguhr was packed round it.

For temperatures below 450° C., the connections were so arranged that there were four circuits in parallel, each circuit containing four lengths of platinum in series. For higher temperatures eight circuits in parallel were used each with two lengths of platinum in series.

After velocity measurements had been made at ordinary temperatures, the furnace was heated up for several days with a current of 6 ampères which raised the temperature of the coil to about 230° C. Before any measurements were made the current was cut off to allow time for the platinum circuits to cool down to the temperature of the coil. The resistance of the sixteen lengths of platinum were then rapidly measured by means of a post-office resistance box and galvanometer in series with a sixteen-way switchboard. These measurements showed that the two outer sections of the coil were cooler than the middle sections. The two end circuits only were therefore heated for some time and the furnace allowed to cool before resistance measurements were again made ; and this heating and cooling were repeated until all sixteen lengths of platinum were of approximately the same resistance. Velocity experiments were then carried out and at the same time temperature readings were taken with the pyrometer; the temperature readings of the outer and inner parts of the coil were found to agree closely. This method of procedure was adopted for determinations of the velocities of sound in nitrogen at temperatures up to 905° C., for methane and carbon dioxide up to 640° C., and for air at 630° C.

The corrections to be applied for the cooler ends of the tube were determined from distance-temperature curves constructed from measurements of temperature at different distances from the ends.

For example, it was found that at one end of the silica tube the full temperature of the furnace (viz., 800° C.) was reached in 25 cm. inwards from the iron wall of the case, and at the other end the full temperature was reached in 23 cm.; thus over a distance of 48 cm. the temperature varied from 20° to 800°. Outside the furnace wall the sound wave had to traverse a total length of 25 cm. kept water cooled at 20°. It was assumed that the sound traversed the cooled portion (25 cm.) at the velocity already determined at 20°, and over the unequally heated 48 cm. at a velocity corresponding to the mean temperature of this portion of the tube, viz., 410°. The values so corrected probably differ from the true velocities by amounts well within the experimental error.

It was assumed that a similar correction was applicable at all temperatures, the actual correction being of course much less at lower temperatures.

In the following Table are given the mean velocities of sound (corrected as above) determined in the silica tube at the temperatures recorded by the resistance thermometers:—

Table IV.—Silica Tube.

Nitrogen.		Carbon dioxide.		Methane.		Air.	
Temperature.	Velocity.	Temperature.	Velocity.	Temperature.	Velocity.	Temperature.	Velocity.
° C.	*m/s.*	° C.	*m/s.*	° C.	*m/s.*	° C.	*m/s.*
18	344·9	18	264·5	15	433·1		
176·5	426·1	196	332·1	194	529·2		
344	502·0	385·4	386·5	390·4	615·1		
365	513·0	632	445·0	640	711·4	630	585·0
539	557·6	634	447·5				
635	596·3						
905	672·5						

After a number of satisfactory results had been obtained for nitrogen, it was decided that determination of the velocity of sound in this gas could conveniently be used as a means of measuring the temperature of the coil.

It was found when a temperature equilibrium had been reached by prolonged heating, that separate charges of nitrogen gave closely concordant results provided both measurements were made within a short time. It was easy, therefore, to fill the coil with another gas and measure the velocity of sound in it between two measurements in nitrogen and be assured that the conditions had not altered appreciably. For instance, on January 15, 1914, after the temperature of the silica tube, as measured by the resistance thermometers, had become constant, the mean of five closely concordant determinations gave the velocity of sound in nitrogen as 519·1 m.p.s. The velocity in the free gas calculated from this is 529·9 m.p.s. and the calculated temperature is 405·4°. The nitrogen was then swept out by carbon dioxide and the mean of seven closely concordant determinations gave the velocity of sound in carbon dioxide as 395·3 m.p.s. On recharging the tube with nitrogen a new set of five determinations gave the velocity of sound in nitrogen as 519·4 m.p.s., from which the velocity in the free gas is calculated as 530·2 m.p.s. and the temperature as 406·1°. A similar set of determinations of the velocity of sound in air made immediately afterwards gave 510·9 m.p.s., from which the velocity in free air is calculated as 521·5 m.p.s. and the temperature 406·3°. It is evident that the conditions had remained practically constant during these experiments, and moreover the values for carbon dioxide so found at different temperatures agreed with those where the temperatures were directly measured. This method was adopted for carbon dioxide and air at 406° and 493° C. with the following results:—

Table V.—Temperatures Calculated from Velocities in Nitrogen.

Carbon dioxide.		Air.	
Temperature.	Velocity.	Temperature.	Velocity.
° C.	*m/s.*	° C.	*m/s.*
405 ·8	395 ·3	406 ·3	510 ·9
493	417 ·3	492 ·7	540 ·8

Similarly by using argon as the standard gas between determinations of nitrogen and of carbon dioxide, and assuming the value of γ for argon to remain constant at 1·667, velocity determinations were made from which the average temperatures of the coil were calculated after applying the necessary corrections. The following results were thus obtained:—

Table VI.—Temperatures Calculated from Velocities in Argon.

Nitrogen.		Carbon dioxide.	
Temperature.	Velocity.	Temperature.	Velocity.
° C.	*m/s.*	° C.	*m/s.*
93·5	386·2	94·1	296·0
95·7	387·4		
522·6	559·1		

The results given in Tables I to VI together with the calculated velocities of sound in argon in the silica tube were then plotted graphically, and curves constructed. From these curves (reproduced on a small scale in fig. 3) the values given in Table VII were read off.

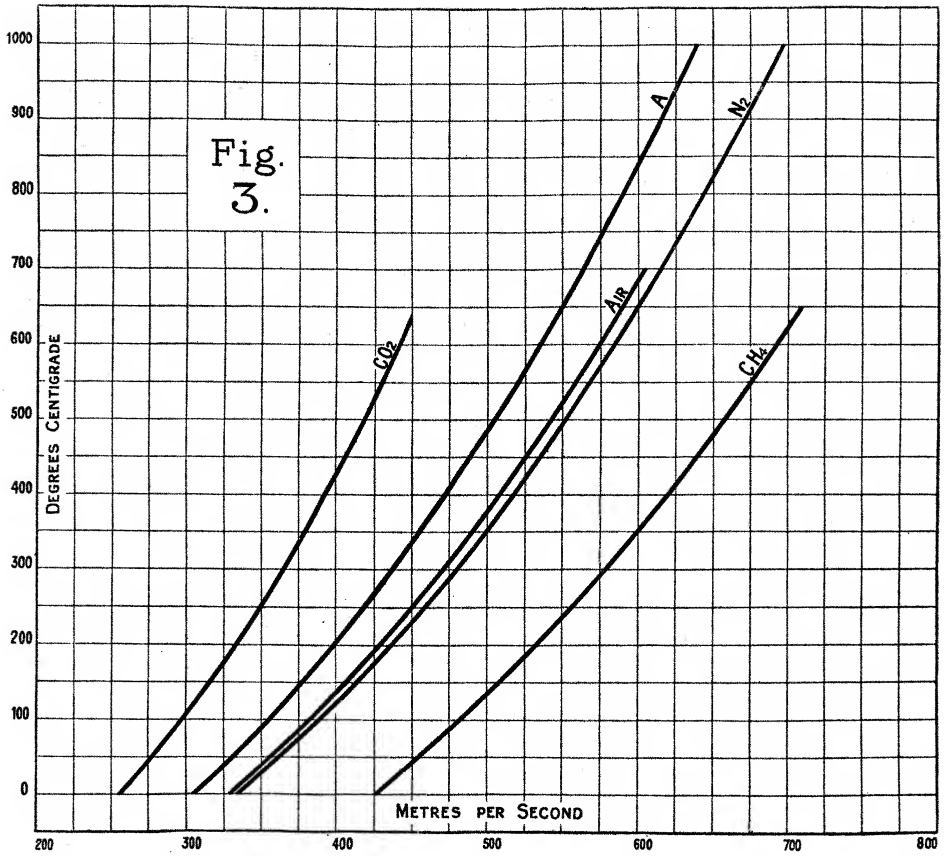

Fig. 3.

Mean velocities of sound in lead, steel, and silica tubes.

Table VII.—Mean Velocities of Sound in Lead, Steel, and Silica Tubes.

Temperature.	Nitrogen.	Argon (calculated).	Air.	Carbon dioxide.	Methane.
° C.	m/s.	m/s.	m/s.	m/s.	m/s.
0	334·4	305·4	328·6	256·6	425·2
100	389·1	355·5	382·5	297·9	481·8
200	436·4	399·0	429·2	333·4	532·5
300	478·6	437·8	470·5	364·7	577·9
400	516·8	472·9	508·1	392·9	618·9
500	551·8	505·5	542·6	419·1	657·2
600	584·3	535·5	574·6	443·0	692·6
700	615·1	563·8	604·6		
800	643·7	590·4			
900	671·0	615·8			
1000	696·8	640·0			

Relation between Velocities of Sound in Tubes and in "Free Gas."

The speed of propagation of sound waves has been found to be smaller in gases contained in narrow tubes than in the open. The observed lowering of velocity is caused partly by the heat exchange between the walls of the tube and the compressed or expanded gas, and partly by friction. Before values of γ can be deduced, the velocities of sound measured in tubes must, therefore, be corrected to velocities in the free gases. The problem has been worked out theoretically by Helmholtz and by Kirchhoff,* who obtained similar mathematical expressions; the only difference consisting in the significance attaching to one of the constants. Both Helmholtz and Kirchhoff represented the velocity of sound in pipes by the expression

$$V' = V\,[1 - c/2r\sqrt{(\pi N)}], \tag{1}$$

in which V is the speed in the free gas and V′ is the velocity of sound of frequency N in a pipe of radius, r. According to Helmholtz the constant, c, is the viscosity of the gas, but according to Kirchhoff c also depends upon the heat exchange between the gas and the wall of the tube and is represented by the expression

$$c = \sqrt{(\mu)} + (V/b - b/V)\sqrt{(\alpha)}, \tag{2}$$

in which V is the velocity of sound in the free gas and b is the Newtonian velocity. μ and α are given by the expressions,

$$\mu = \eta/\rho, \qquad \text{and} \qquad \alpha = k/\rho c_v,$$

where η is the coefficient of viscosity, k the coefficient of conductivity, ρ the density of the gas and c_v the specific heat at constant volume. Substituting the above values of μ and α in (2),

$$c = \sqrt{(\eta/\rho)} + \sqrt{(k/\rho c_v)}\,(V/b - b/V).$$

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* 'Pogg. Ann.,' vol. 134, p. 177 (1868).

Substituting $k = 1{\cdot}6027\,\eta c_v$,[*] then

$$c = \sqrt{(\eta/\rho)}\,[1+\sqrt{(1{\cdot}6027)}\,(\mathrm{V}/b-b/\mathrm{V})\,] \quad \text{but} \quad \mathrm{V}/b = \sqrt{(\mathrm{C}_p/\mathrm{C}_v)} = \sqrt{(\gamma)},$$

so that
$$c = \sqrt{(\eta/\rho)}\,\{1+\sqrt{(1{\cdot}6027)}\,[(\gamma-1)/\sqrt{(\gamma)}]\,\}. \tag{3}$$

This expression may be used to calculate the variation of c with temperature for any given gas. According to Sutherland,[†] the variation of the viscosity of a gas with temperature is represented by the expression

$$\eta_t = \eta_0\,\frac{1+\mathrm{C}_1/273}{1+\mathrm{C}_1/\mathrm{T}}\sqrt{(1+t/273)}, \tag{4}$$

where C_1 is a constant for the particular gas under consideration, t the temperature in degrees centigrade, and T the temperature on the absolute scale. Considering the case of a perfect gas,

$$\rho_t = \rho_0\,.\,273/\mathrm{T},$$

so that by substitution in (3)

$$c = \sqrt{\left(\frac{\eta_0\mathrm{T}\,(1+\mathrm{C}_1/273)\sqrt{(1+t/273)}}{\rho_0\times 273\,(1+\mathrm{C}_1/\mathrm{T})}\right)}\,\{1+\sqrt{(1{\cdot}6027)}\,[\,(\gamma-1)/\sqrt{(\gamma)}]\}. \tag{5}$$

Several investigations have been carried out with the object of testing the validity of the Kirchhoff expression (1). Schneebeli[‡] and Seebech[§] obtained values supporting the Helmholtz and Kirchhoff theories as to the variation of velocity with the diameter of the pipe, but their results were not in agreement with the theoretical dependence of velocity on the frequency of the note employed. From experiments carried out by the method of dust figures in tubes varying in diameter from 25 mm. to 80 mm., Kaiser concluded that the velocity of sound varied with the pitch of the note and the diameter of the pipe, according to the Kirchhoff expression, provided that a higher value than the theoretical be assigned to the constant, c. It is to be observed that Kirchhoff himself had pointed out that the value of c would be greater than theoretical if the surface of the tube were not perfectly smooth. Blaikley,[||] using brass organ pipes of a special shape, obtained results which supported the theory with regard to the effect of the frequency of the note and the diameter of the pipe. On the other hand, Müller[¶] and Schulze came to the conclusion that the Kirchhoff expression had no general validity and that the velocity in tubes depends on the material.

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[*] O. E. Meyer, 'The Kinetic Theory of Gases.'

[†] 'Phil. Mag.,' vol. 36, p. 507 (1893).

[‡] 'Pogg. Ann.,' vol. 136, p. 296 (1869).

[§] 'Pogg. Ann.,' vol. 139, p. 104 (1870).

[||] 'Phil. Mag.,' vol. 16, p. 447 (1883); p. 328 (1884).

[¶] 'Ann. d. Physik,' vol. 2, p. 331 (1903).

From the results of the above-mentioned investigations, it may be concluded that the dependence of velocity on diameter, but not on the frequency of the note employed, is represented by the Kirchhoff formula. The constant is found to be greater than the theoretical value of c, its exact value varying with the material of the tube.

In the experiments described in this paper, the same note was used for experiments in the same tube and the results in the different tubes were in close agreement. For these experiments the expression

$$V' = V[1-c/2r\sqrt{(\pi N)}]$$

may therefore be simplified to

$$V' = V(1-Kc), \tag{6}$$

in which K is a constant embodying the effect of the frequency of the note, the diameter, material, and shape of the tubes. The theoretical constant, c, varies with the gas used and the temperature according to equation (5). If the value of Kc be known for one gas at a given temperature, then its magnitude may be calculated for any other gas at any other temperature. The following values of the Kirchhoff constant, c, for nitrogen, argon, air, and carbon dioxide at different temperatures have been calculated from equation (5).

Table VIII.

Gas.	Nitrogen.	Argon.	Air.	Carbon dioxide.
$\rho_0 \times 10^3$	1·2507	1·7809	1·2928	1·9768
$\eta_0 \times 10^4$	1·674	2·10	1·733	1·414
Sutherland constant C_1	109	160	119·4	277
Temperature, ° C.	Kirchhoff constant, c.			
0	0·52	0·57	0·52	0·36
100	0·69	0·76	0·69	0·48
200	0·84	0·93	0·84	0·59
300	0·99	1·10	0·99	0·69
400	1·12	1·26	1·13	0·79
500	1·26	1·42	1·27	0·88
600	1·38	1·57	1·39	0·97
700	1·51	1·72	1·52	
800	1·62	1·86		
900	1·74	2·00		
1000	1·85	2·13		

Since the Sutherland constant has not been determined for methane, the values of the Kirchhoff constant, c, for this gas at different temperatures have been calculated from the simpler expression of O. E. Meyer and v. Obermeyer.

$$\eta_t = \eta_0 (1+\beta t).$$

In the case of ethane, the viscosities have been assumed to be $1{\cdot}03 \times 10^{-4}$ at 10° C., $1{\cdot}15 \times 10^{-4}$ at 50° C., and $1{\cdot}30 \times 10^{-4}$ at 100° C.

Table IX.

Methane.	
$\rho_0 \times 10^3$	0·7171
$\eta_0 \times 10^4$	1·040
β	0·003
Temperature, ° C.	Kirchhoff constant, *c*.
0	0·51
100	0·64
200	0·78
300	0·91
400	1·04
500	1·17
600	1·30
Ethane.	
$\rho_0 \times 10^3$	1·3906
Temperature, ° C.	Kirchhoff constant, *c*.
10	0·34
50	0·38
100	0·44

Recent determinations of the velocity of sound in free nitrogen, and calculations from accepted values of γ, lead to the conclusion that the velocity of sound in free nitrogen at 0° C. is probably 337·5 metres per second. Substituting this value of the velocity and the calculated Kirchhoff constant, 0·52, in equation (6), the constant K for the tubes used is found to be practically the same for the three tubes, viz., 0·018.

Equation (6) then becomes

$$V' = V(1-0{\cdot}018c).$$

From this expression the velocities of sound given in Table VII have been corrected to velocities in the free gases, and the following results obtained (Table X):—

Table X.

Temperature.	Velocities of sound in free gas in metres per second.				
	Nitrogen.	Argon (calculated).	Air.	Carbon dioxide.	Methane.
° C.					
0	337·5	308·5	331·8	258·3	429·2
100	394·1	360·3	387·5	300·4	487·4
200	443·1	405·7	435·8	336·9	540·0
300	487·2	446·5	479·0	369·3	587·3
400	527·3	483·9	518·6	398·6	630·8
500	564·5	518·6	555·2	425·7	671·4
600	599·4	551·1	589·3	450·9	709·2
700	632·2	581·7	621·6		
800	663·0	610·9			
900	692·4	638·7			
1000	720·6	665·5			

Temp., ° C.	Ethane.
10	307·7
50	327·4
100	349·3

The relationship existing between the molecular heat values of a gas at constant pressure and constant volume are expressed in the two following equations, developed by E. Warburg from Berthelot's equation of state:—*

(a) $$C_p - C_v = R\,(1+\pi \,.\, 9/128 \,.\, 24\tau^3),$$

(b) $$C_p/C_v = \frac{V^2M}{RT}\,[1-\pi \,.\, 9/128 \,.\, 2\tau(1-6\tau^2)\,],$$

in which $\pi = p/p_x$, p = pressure, p_x = critical pressure; $\tau = T_x/T$, T = temperature (absolute), T_x = critical temperature (absolute); R in (a) = 1·985 and (b) = 82·07 × 1033·3 × 981·183; V is the velocity of sound in centimetres per second and M is the molecular weight of the gas.

From the two equations (a) and (b), and the velocities of sound given in Table X, the molecular heats of the gases under consideration have been calculated in Tables XI to XV.

It is obvious that the specific heats of nitrogen and of air rise fairly regularly with the temperature, the values for equal increments of temperature falling nearly on a straight line between 0° and 700°. Between 700° and 1000° the values found for nitrogen are more irregular, as might be expected, the value at 800° being probably too high and that at 1000° too low. In Table XII the values of C_v for nitrogen are calculated from the expression:—

$$C_v = 4{\cdot}82 + 0{\cdot}00024T + 0{\cdot}00000013T^2.$$

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* Nernst, 'Theoretische Chemie,' 7. aufl., s. 245.

Table XI.—Nitrogen.

Temperature.	M = 28·02.	p_x = 33·0.	T_x = 127.	C_v calculated from 4·775 + 0·00042T.
	$C_p - C_v$.	C_p/C_v.	C_v.	
° C.				
0	1·9952	1·408	4·890	4·890
100	1·9900	1·404	4·926	4·932
200	1·9870	1·400	4·968	4·974
300	1·9862	1·396	5·014	5·016
400	1·9857	1·392	5·066	5·058
500	1·9855	1·389	5·104	5·100
600	1·9853	1·386	5·143	5·142
700	1·9853	1·383	5·184	5·184
800	1·9852	1·379	5·238	5·226
900	1·9851	1·376	5·280	5·268
1000	1·9850	1·374	5·308	5·310

Table XII.

Temperature.	C_v found.	C_v (calculated).
° C.		
0	4·890	4·896
100	4·926	4·928
200	4·968	4·963
300	5·014	5·001
400	5·066	5·041
500	5·104	5·084
600	5·143	5·129
700	5·184	5·177
800	5·238	5·228
900	5·280	5·280
1000	5·308	5·336

The values deduced from our experiments on nitrogen are lower than those calculated by Bjerrum and those recently given by Tizard and Pye.*

Table XIII.—Carbon Dioxide.

Temperature.	M = 44·005.	p_x = 73·0.	T_x = 304.	C_v calculated from 6·1 + 0·0028T.	C_v calculated from 6·30 + 0·00205T + 0·0000007 T^2.
	$C_p - C_v$.	C_p/C_v.	C_v.		
° C.					
0	2·0484	1·296	6·920	6·864	6·912
100	2·0098	1·281	7·152	7·144	7·160
200	1·9972	1·270	7·397	7·424	7·427
300	1·9919	1·260	7·658	7·704	7·705
400	1·9892	1·249	7·989	7·984	7·997
500	1·9878	1·240	8·282	8·264	8·303
600	1·9870	1·230	8·639	8·544	8·623

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* 'Automobile Eng.,' February and March, 1921.

The variation of C_v with temperature for carbon dioxide may therefore be represented approximately by the expression

$$C_v = 6{\cdot}1 + 0{\cdot}0028T,$$

or, more accurately, by the expression,

$$C_v = 6{\cdot}30 + 0{\cdot}00205T + 0{\cdot}0000007T^2.$$

The values found by us for carbon dioxide are also lower than those calculated by Bjerrum and by Tizard and Pye.

Table XIV.—Methane.

Temperature.	M = 16·037.	p_x = 50·0.	T_x = 177·5.	C_v calculated from 6·66 + 0·019t.
	$C_p - C_v$.	C_p/C_v.	C_v.	
° C.				
0	2·0034	1·301	6·656	6·66
100	1·9922	1·228	8·738	8·56
200	1·9885	1·188	10·577	10·46
300	1·9870	1·160	12·419	12·36
400	1·9862	1·139	14·288	14·26
500	1·9858	1·124	16·015	16·16
600	1·9856	1·111	17·883	18·06

The above results, which show a rapid increase in the value C_v with rise of temperature for methane over the range experimented on, may be represented approximately by the equation

$$C_v = 6{\cdot}66 + 0{\cdot}019t \text{ at } t^\circ \text{ Centigrade.}$$

It is to be noted that methane begins to decompose, giving hydrogen and carbon, at a temperature of 700° C. in a silica tube.

Table XV.—Ethane.

Temperature.	M = 30·058.	p_x = 50·2.	T_x = 307.
	$C_p - C_v$.	C_p/C_v.	C_v.
° C.			
10	2·0685	1·224	9·22
50	2·0420	1·208	9·82
100	2·0222	1·186	10·87

The values of C_v for ethane between 10° and 100° may therefore be represented by the expression

$$C_v = 9{\cdot}04 + 0{\cdot}0183t \text{ at } t^\circ \text{ C.}$$

The expressions representing the molecular heats at constant volume and different temperatures of the gases considered in this paper are grouped

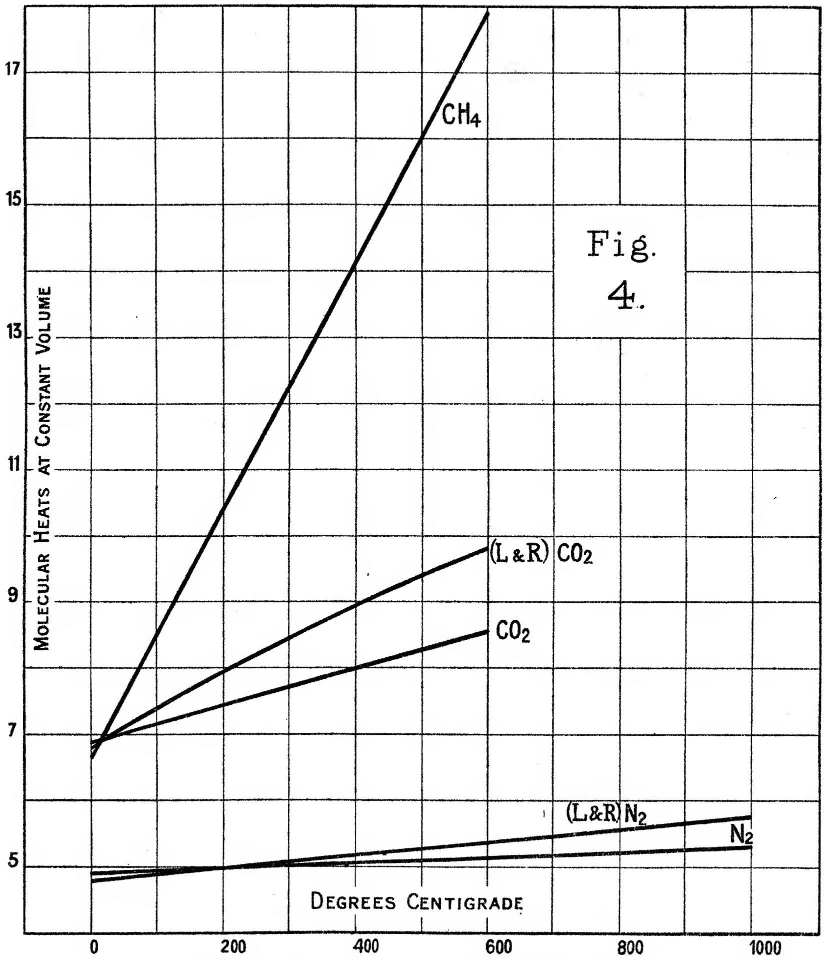

Fig. 4.

Molecular heats of gases at constant volume.

Table XVI.—Variation of C_v with Temperature at T° abs. or t° C.

Gas.	Temperature range.	C_v.	C_v (Lewis and Randall).
	° C.		
Nitrogen	0–1000	$4\cdot775 + 0\cdot00042\,T$	$4\cdot5 + 0\cdot001\,T$
Air	0–700	$4\cdot8 + 0\cdot0004\,T$	$4\cdot5 + 0\cdot001\,T$
Carbon dioxide	0–600	$6\cdot30 + 0\cdot00205\,T$ $+ 0\cdot0000007\,T^2$	$5\cdot0 + 0\cdot0071\,T$ $- 0\cdot00000186\,T^2$
Methane	0–600	$6\cdot66 + 0\cdot019\,t$	
Ethane.................	0–100	$9\cdot04 + 0\cdot0183\,t$	

together in Table XVI and compared with those deduced by Lewis and Randall.[*] They are also shown graphically in fig. 4 (p. 25).

Previous determinations of C_p/C_v for methane at approximately 20° C. by Mason,[†] Müller,[‡] and Capstick[§] give a mean value of 1·313, which is rather higher than that obtained from the experiments described in this paper; although Lussana[||] obtained a value of 9·464 for C_p from 0° C. to 100° C., which is in good agreement with the authors' figure of 9·606.

In the case of ethane, Daniell and Pierron[¶] and Capstick[**] obtained values of 1·22 and 1·182 respectively for the ratio of the two specific heats at ordinary temperature, as against the authors' value of 1·221 at 15° C.

We have to thank those research students who gave us assistance during the earlier stages of this investigation, and in particular Messrs. W. H. Bentley, D.Sc., F. Fairbrother, M.Sc., and H. Henstock, Ph.D.

The authors regret the unavoidable delay—due to the war—in presenting the results of these experiments, most of which were carried out during the years 1912 to 1915. They wish to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for a grant towards the expense of the apparatus employed, and to the Council of the Chemical Society for a grant towards the cost of the chemicals used.

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[*] 'Journ. Amer. Chem. Soc.,' vol. 34, p. 1128 (1912).

[†] 'Ann. Chim. Phys.' [3], vol. 53, p. 277 (1858).

[‡] Müller, 'Wied. Ann.,' vol. 18, p. 95 (1883).

[§] 'Roy. Soc. Proc.,' vol. 54, p. 101 (1893).

[||] 'Nuovo Cimento' [3], vol. 5, pp. 70, 130 (1896); vol. 7, pp. 61, 365 (1898).

[¶] 'Bull. Soc. Chim.' [3], vol. 21, p. 801 (1899).

[**] 'Roy. Soc. Proc.,' vol. 54, p. 101 (1893).

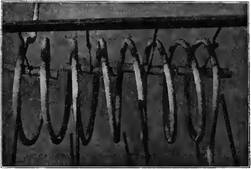

Fig. A.—Wound silica tube, showing method of suspension before kieselguhr was packed round it.